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Activity Enhancement of CuZn-impregnated FSM-16 by Modification with 1,3-Butanediol for Steam Reforming of Methanol[1]

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Abstract—Catalytic activities of CuZn-impregnated FSM-16 catalysts, prepared by the conventional impregnation method and a modified impregnation method with 1,3-butanediol, in steam reforming of methanol were examined. The catalytic activity of the modified CuZn-impregnated FSM-16 was remarkably higher than that of the one prepared by the conventional impregnation method. Characterization of the catalysts by XRD and TPR showed that the enhancement in catalytic activity is due to an improvement in copper dispersion. The amount of 1,3-butanediol, the calcination temperature, and the amount of metal loading were varied to seek the optimal catalyst with the highest methanol conversion. Besides 1,3-butanediol, other organic compounds such as 1,3-propanediol, ethylene glycol, and citric acid also resulted in an enhancement in catalytic activity, while propanol did not.

1. INTRODUCTION

Mesoporous materials such as MCM-41 [1] and FSM-16 [2] having large highly ordered pores and high surface area have attracted much interest in the field of adsorption and catalytic chemistry. Many researchers [3–9] have used these materials as a catalyst support for some transition metals due to its specific properties. There are many ways to introduce metals into these mesoporous materials, for instance, ion exchange, impregnation, and encapsulation of metal ions to the structure during synthesis. Techniques such as ion exchange and encapsulation can result in more active catalysts than the impregnation technique [4]. However, in ion exchange and encapsulation techniques, a large amount of metal cannot be introduced to the support and the preparation methods are more complicated. On the other hand, the impregnation method is very convenient, but the impregnated catalyst has a low metal dispersion, which consequently results in a low activity. Therefore, improvement of impregnation technique is necessary.

Polydentate or bidentate organic compounds can affect the hydrolytic polymerization of metal ions by the chelate effect [10]. It was reported that organic complexing agents were used in the sol-gel method to control the physical properties of the gel [11–14] and were used to control the structure of the metal oxide [15, 16]. In this study, we used 1,3-butanediol (1,3-BD) as a modifier to control the dispersion of copper and zinc impregnated into FSM-16. The catalytic activity and stability of the catalysts in steam reforming of methanol were examined. Furthermore, the effect of other organic compounds such as 1,3-propanediol (1,3-PD), ethylene glycol (EG), citric acid, and propanol on the activity of the catalyst was also investigated in this report.

2. EXPERIMENTAL

2.1. Catalyst Preparation

An FSM-16 type mesoporous molecular sieve in silicate form was prepared according to the procedure described in our previous report [17]. The supported FSM-16 catalysts were prepared by two methods: a conventional wet impregnation method and a modified impregnation method with organic compounds.

In the conventional impregnation method, a solution of copper nitrate and zinc nitrate (mole ratio of 7 : 3) and a solution of copper sulfate and zinc sulfate were used for impregnation. The metal salt solutions were mixed with FSM-16, and the mixture was kept at room temperature for 1 h. After impregnation, the catalysts were dried at 383 K for 1 h and then calcined in air at 773 K for 3 h. The catalysts were denoted as CuZn–NO_3/FSM-16 and CuZn–SO_4/FSM-16, respectively.

In the modified impregnation method, the catalysts were prepared in almost the same way as in the conventional impregnation method, except 2.7–18.6 × 10^{-4} mol/g Cat of 1,3-butanediol (1,3-BD) was added to the copper nitrate and the zinc nitrate solution prior to impregnation. The catalysts were denoted

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Table 1. Steam reforming of methanol on various CuZn-impregnated FSM-16

Catalyst*	Reaction temperature, K	Amount of 1,3-butanediol, 10^{-4} mol/g Cat	Methanol conversion, mol %	Selectivity to CO_2, mol %
CuZn-SO_4/FSM-16	573	0	0	–
CuZn-NO_3/FSM-16	573	0	36.8	92.9
″	503	0	0	–
CuZn-BD/FSM-16-*1*	503	2.7	39.7	100
CuZn-BD/FSM-16-*2*	503	5.3	59.5	100
CuZn-BD/FSM-16-*3*	503	8.0	41.4	100
CuZn-BD/FSM-16-*4*	503	9.3	27.8	100
″	573	9.3	100	96.9
CuZn-BD/FSM-16-*5*	503	18.6	28.3	100

* Metal content (Cu + Zn) = 10 wt %; Cu : Zn = 7 : 3; catalysts were calcined at 773 K for 3 h.

CuZn–BD/FSM-16. The modified catalysts were calcined at 483–773 K, and the metal content was varied from 10–25 wt %. Furthermore, in order to study the effect of the other organic compounds on the performance of the catalyst, propanol, 1,3-propanediol (1,3-PD), ethylene glycol (EG), and citric acid were also used instead of 1,3-BD in this report.

2.2. Catalytic Test and Product Analysis

The steam reforming of methanol was carried out in a conventional fixed-bed flow reactor under the following conditions: reaction temperature, 503 K; flow rate of carrier gas (He), 50 ml/min; catalyst loading, 50 mg; methanol and water inlet pressure (H_2O/methanol = 1.88 molar ratio), 1.6 and 3.0 kPa, respectively; W/F = 0.060 (g Cat s)/cm^3. Prior to the reaction, the catalyst was reduced at 573 K for 1 h in a flow of pure hydrogen at a rate of 50 ml/min and then cooled down to the reaction temperature. All gases were controlled by mass flow controllers. The gas products were analyzed by GC-TCD with two columns of PEG-1000 and activated carbon.

2.3. Characterization

X-ray diffraction (XRD) was conducted with a Shimadzu XRD 6000, using CuK_α radiation, a step size of 0.02°, and a scan rate of 2θ with 2 deg/min from 2° to 10° of 2θ and from 10° to 80° of 2θ. The reduction properties of the catalysts were measured by the temperature-programmed reduction (TPR) method. About 0.100 g of the calcined catalyst was placed in a quartz reactor. Argon was first passed through the sample until the baseline recorded by TCD was stable, then the sample was reduced up to 773 K in a gas mixture consisting of 5% H_2–95% Ar at a heating rate of 5 K/min. The reduction signal was detected by TCD.

3. RESULTS AND DISCUSSION

3.1. Effect of Metal Salt and Amount of 1,3-BD on the Catalytic Activity

Catalytic activities in steam reforming of methanol over various CuZn-impregnated FSM-16 are shown in Table 1. From Table 1, it was found that the anion type of metal salt affected the catalytic activity. Methanol conversion at 573 K of the catalyst prepared by copper and zinc nitrate was 36.8% higher than the catalyst prepared by copper and zinc sulfate. This distinct difference in methanol conversion can be explained in terms of acidity. It was reported that sulfate ions can increase the acidity of the catalyst by changing weakly acidic surface silanol groups to Brønsted acid sites [18]. Steam reforming of methanol is a base-catalyzed reaction; therefore, an increase in acidity results in a decrease in activity.

As seen in Table 1, all CuZn–BD/FSM-16 catalysts show higher methanol conversion than CuZn–NO_3/FSM-16. Adding only a small amount of 1,3-BD (2.7×10^{-4} mol/g Cat) resulted in an increase in methanol conversion from 0 to 39.7% at 503 K. This result reveals that adding 1,3-BD to the solution before impregnation results in a remarkable enhancement of activity. The methanol conversion ability of CuZn–BD/FSM-16 is dependent on the amount of 1,3-BD, as shown in Fig. 1. An increase in the amount of 1,3-BD from 2.7×10^{-4} to 5.3×10^{-4} mol/g Cat resulted in an increasing in methanol conversion. However, a further

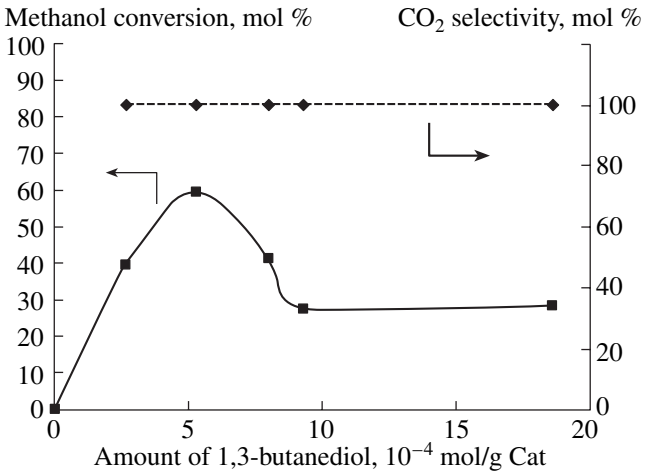

Fig. 1. Effect of amount of 1,3-butanediol on the methanol conversion and CO_2 selectivity.

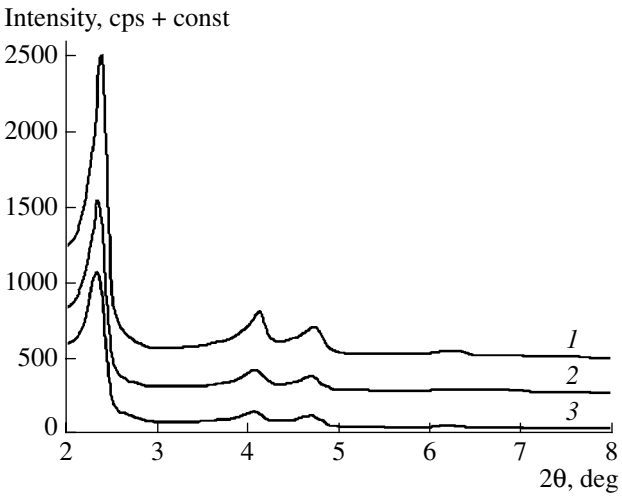

Fig. 2. XRD patterns of (*1*) FSM-16, (*2*) CuZn–NO_3/FSM-16, and (*3*) CuZn–BD/FSM-16-2.

increase in the amount of 1,3-BD resulted in a decrease in methanol conversion. From Fig. 1, the maximum methanol conversion was obtained at 5.3×10^{-4} mol/g Cat of 1,3-BD.

As for the selectivity of the catalysts, CO_2 was the only carbon product observed at 503 K. In our experiment, helium was used as the carrier gas, providing acceptable sensitivity for carbon oxides. It should be noted that high selectivity observed here would result from low concentration of methanol. At not overly high temperatures, methanol decomposition does not preferentially occur; thus, CO_2 can be produced by just the reverse water gas shift reaction. The possibility of the reverse water gas shift reaction here was very low because of the low content of methanol in the feed, and this provided a low concentration of CO_2 and H_2 as well. At a higher temperature, the possibility of methanol decomposition and reverse water gas shift reaction became higher. A small amount of CO was observed at 573 K. At 573 K, the methanol conversion of CuZn–BD/FSM-16-4 is 100% and the selectivity to CO_2 is 96.9%, which is 4% higher than the selectivity to CO_2 of CuZn–NO_3/FSM-16. This suggests a slight improvement in selectivity to CO_2. The slight difference in selectivity would be due to different surface structure of Cu planes.

XRD measurements were performed to characterize the physical properties of the catalysts in order to explain the enhancement in methanol conversion. Figure 2 shows the XRD patterns of FSM-16, CuZn–NO_3/FSM-16, and CuZn–BD/FSM-16-2 at small angles (2°–10° 2θ). The four peaks in Fig. 2 are characteristic peaks of the hexagonal array of FSM-16. The XRD patterns of CuZn–NO_3/FSM-16 and CuZn–BD/FSM-16-2 are similar to the pattern of FSM-16, suggesting there was no major change in the structure. However, the intensity of the observed peaks became relatively lower. This indicates that there was a partial loss of the impregnated catalysts' ordered structure during preparation. At large angles (10°–60° 2θ), the XRD patterns were obtained to examine the dispersion state of Cu species and are shown in Fig. 3. The XRD spectra exhibit a broad band at around $2\theta = 22°$ and two peaks at $2\theta = 35.5°$ and $2\theta = 38°$, which can be attributed to the amorphous silicate structure, CuO(111) and CuO(200) phase, respectively. From Fig. 3, it is clear that the CuO peaks of CuZn–NO_3/FSM-16 are sharper and higher in intensity than those of CuZn–BD/FSM-16 catalysts. This suggests that the CuO crystallites' size in CuZn–NO_3/FSM-16 was larger than that in the CuZn–BD/FSM-16 samples. The CuO peaks for CuZn–BD/FSM-16-1 and -2 were not observed due to their poor and highly disordered crystallization. This suggests the high dispersion of CuO in the catalysts. For CuZn–BD/FSM-16-3–5, the CuO peaks were broad and their intensity increased with an increasing amount of 1,3-BD, suggesting that a surplus amount of 1,3-BD would reduce the dispersion. This result corresponds to the methanol conversion data shown in Table 1.

The reduction properties of the copper oxides from the different samples were examined by temperature-programmed reduction (TPR) with hydrogen. The reduction results are shown in Fig. 3. All the samples exhibit a broad band in the temperature range 473–573 K which can be ascribed to the reduction of Cu^{2+} to Cu^0. For CuZn–NO_3/FSM-16, the reduction peak is centered at 523 K, and the reduction is completed at around 573 K. On the other hand, the reduction peak of the CuZn–BD/FSM-16-1 sample appears at 503 K, and the reduction is completed at around 543 K. The shift of the reduction peak to a lower temperature indicates the improvement in reducibility by 1,3-BD. The reducibility of the catalysts is affected by the amount of 1,3-BD impregnated in the support. The CuZn–BD/FSM-16-2 exhibits the lowest reduction temperature among all

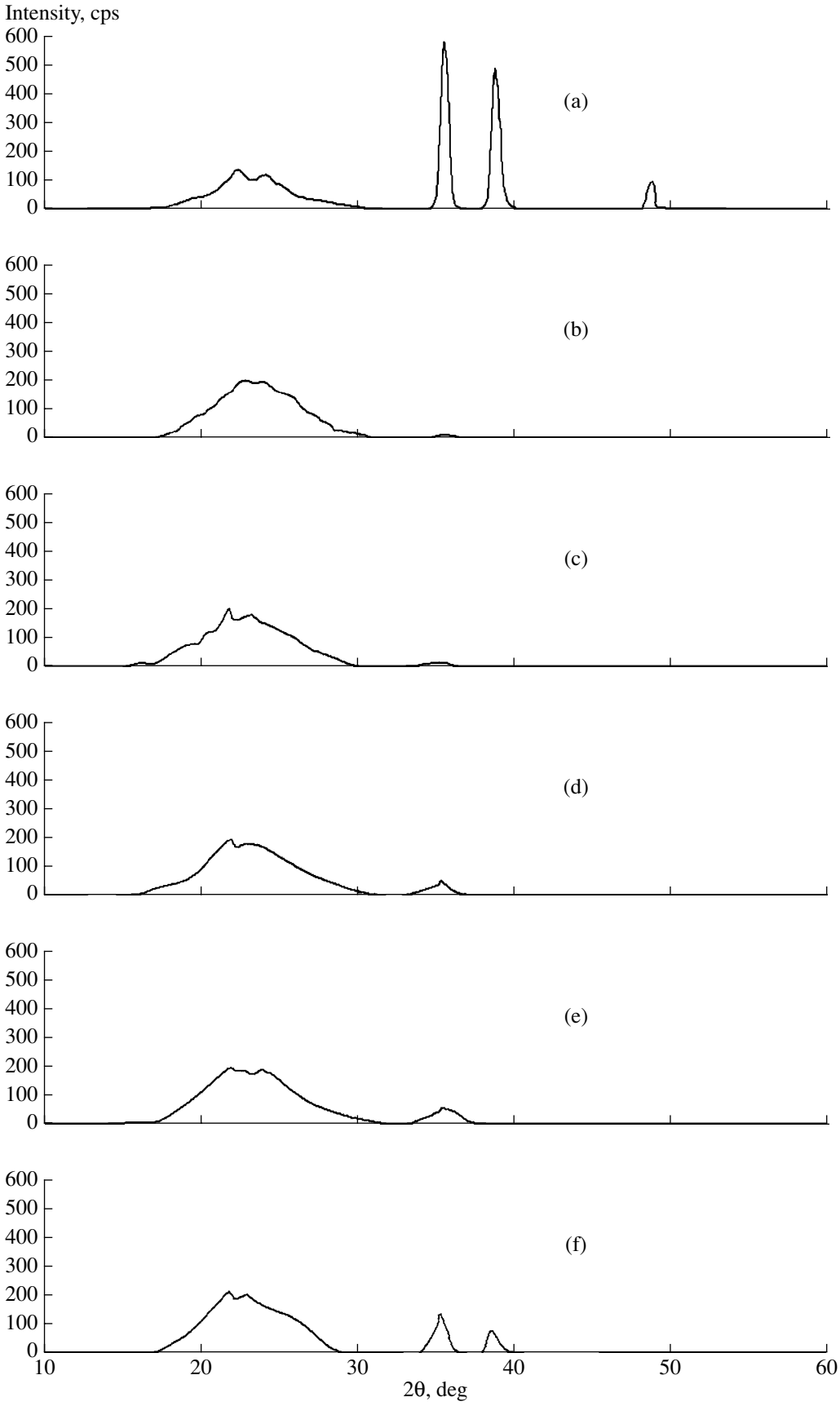

Fig. 3. XRD patterns of (a) CuZn–NO_3/FSM-16 and (b–f) CuZn–BD/FSM-16-1–5 at large angles.

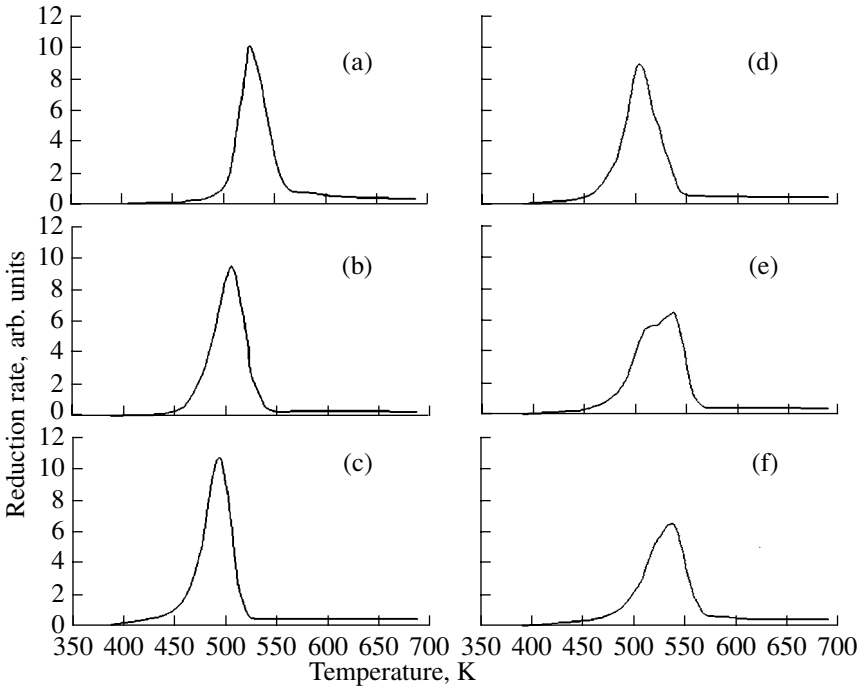

Fig. 4. TPR profiles of CuZn-impregnated catalysts: (a) CuZn–NO_3/FSM-16, (b–f) CuZn–BD/FSM-16-1–5, respectively.

CuZn–BD/FSM-16 catalysts. The TPR peaks for CuZn–BD/FSM-16-3–5 are broader and have lower intensity than that of the other samples. There are also shoulders and splits, which are probably due to the presence of difference states of CuO. For CuZn–BD/FSM-16-3–5 samples, the reduction peaks shift to higher temperatures with an increase in the amount of 1,3-BD. The enhancement in reducibility of CuZn–BD/FSM-16 catalysts suggests a lower crystallinity and higher dispersion of CuO impregnated in FSM-16 than that in CuZn–NO_3/FSM-16. The TPR result is consistent with XRD and methanol conversion results. This is also in good agreement with the literature in that catalysts with lower copper-reduction temperatures showed higher activity for methanol conversion at low temperatures [19, 20].

From the above results, XRD and TPR data show that the enhancement in methanol conversion of the modified catalysts with 1,3-BD was due to the improvement in the dispersion state of the Cu species impregnated in the FSM-16 support.

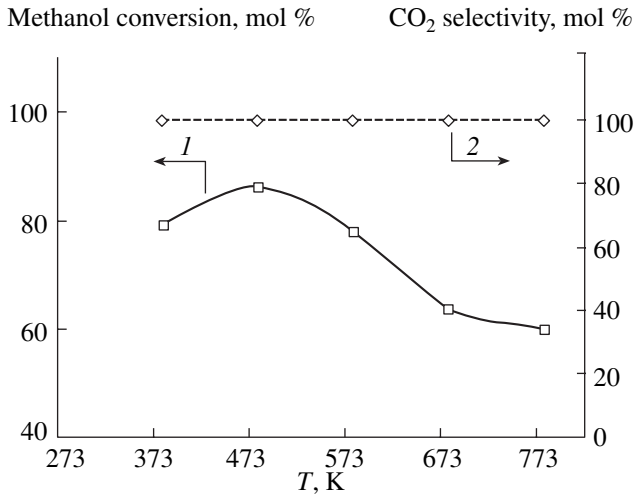

Fig. 5. (*1*) Methanol conversion and (*2*) CO_2 selectivity of CuZn–BD/FSM-16-2 (*1*) uncalcined (left-hand data) and (*2*) calcined at different temperatures.

3.2. Effect of Calcination Temperature on Catalytic Activity

Figure 5 illustrates the effect of calcination temperature on the activity of CuZn–BD/FSM-16-2. The maximum methanol conversion was obtained using the catalyst calcined at 473 K. Figure 6 shows the XRD patterns of the catalysts. The catalysts calcined at 473–673 K exhibit no CuO peak because the CuO particles are amorphous and their crystallite size is below the detection limit of XRD. Although the differences between catalysts calcined at 493–773 K cannot be observed by XRD measurement, the lower methanol conversion of the catalysts calcined at high temperatures (573–773 K) relative to those calcined at low temperature (493 and 383 K) would be due to sintering of copper species during oxidation by air. It is generally known that copper is a tender metal and would sinter easily at temperatures >573 K. Methanol conversion of the catalyst calcined at 473 K was the highest because the sintering of copper

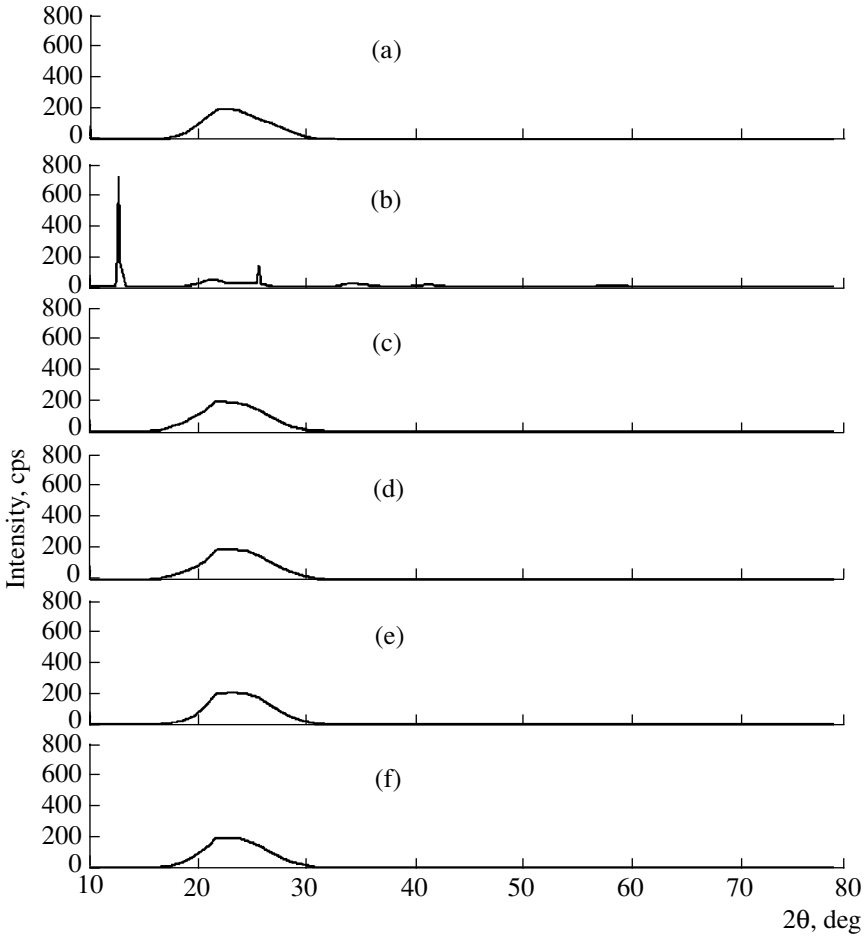

Fig. 6. XRD patterns of (a) CuZn–NO_3/FSM-16 not calcined and (b–f) CuZn–BD/FSM-16-2 (b) not calcined and (c–f) calcined at 473–773 K, respectively.

would not preferentially occur at this temperature. The methanol conversion of the uncalcined catalyst was also higher than that of the catalysts calcined at >573 K. This suggests that the catalyst did not need to be oxidized to CuO before being reduced and used in the methanol steam reforming reaction. Further measurements of metal particles are needed to elucidate the effect of calcination temperature.

To study the impact of the impregnation step, which is expected to determine the final active component in the support, XRD measurement of the uncalcined catalyst was performed. The XRD pattern of uncalcined CuZn–BD/FSM-16-2 is totally different from the calcined samples and uncalcined CuZn–NO_3/FSM-16. The XRD pattern of the uncalcined CuZn–BD/FSM-16-2 exhibits peaks at $2\theta = 12.73°$ and $2\theta = 25.7°$, which is close to (003) and (006) reflections of the layer ordering in the *C*-axis direction of a layer double hydroxide [20, 21]. These XRD peaks suggest the occurrence of a crystal-like structure in the CuZn–BD/FSM-16-2 sample. It is generally acknowledged that Cu^{2+} salts dissolve readily in water and give aqua ions. The addition of a ligand to such an aqueous solution leads to the formation of complexes by successive displacement of water molecules [22]. Therefore, it is assumed in this study that 1,3-BD probably replaced the water around metal ions and resulted in the formation of the crystal-like structure observed in the XRD pattern of the uncalcined sample.

3.3. Effect of Metal (Cu + Zn) Loading on the Catalytic Activity

Figure 7 shows the effect of metal (Cu + Zn) loading on the methanol conversion. All the catalysts were calcined at 473 K. The conversion increased with an increase in the metal loading, and the maximum conversion was obtained at 22 wt % metal loading. The XRD patterns of the catalysts with various metal loadings are shown in Fig. 8. At 10, 15, and 19 wt % metal, CuO peaks were not observed, while, at high metal loading (22 and 25 wt %), the peaks of CuO(111) and CuO(200) were observed. Their intensities became higher with an increase in metal loading. This indicates an increase in the crystallite size of CuO with an increase in metal loading. It is interesting to note that the XRD patterns of the catalysts with 22 and 25 wt %

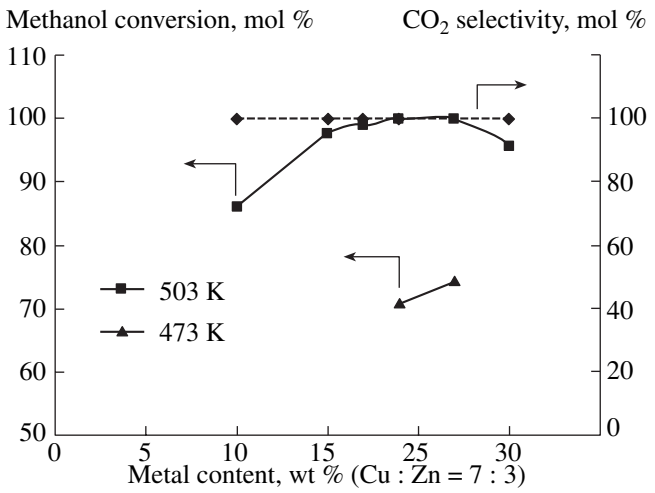

Fig. 7. Effect of metal loading on the methanol conversion and CO_2 selectivity.

metal loading also exhibit a peak at $2\theta = 12.7°$, which suggests the presence of the crystal-like structure that was observed in the uncalcined sample. This implies that, at high metal loading, all the Cu species were not oxidized to CuO at 473 K. However, these unoxidized Cu species would be reduced to metallic Cu during reduction pretreatment before the steam reforming reaction.

3.4. CuZn–BD/FSM-16-2 Stability

The stability of CuZn–BD/FSM-16-2 with 15.4 wt % Cu and 6.4 wt % Zn during steam reforming of methanol was investigated over a 24-h period on steam at an operating temperature of 503 K and the result is shown in Fig. 9. A minor drop in methanol conversion was observed after 10 h. The drop was slow and seemed to become stable in the long run. The decrease in methanol conversion was due to the sintering of copper as shown by XRD (not shown here). The partial pressure of methanol or water may affect the stability of the catalyst. However, further study over a long period and higher partial pressure of the reactants are needed to elucidate the stability of CuZn–BD/FSM-16-2.

3.5. The Effect of the Impregnated Organic Compound on Catalytic Activity

Table 2 shows the methanol conversion and selectivity to CO_2 of the CuZn-impregnated FSM-16 modified with various kinds of organic compounds. It can be

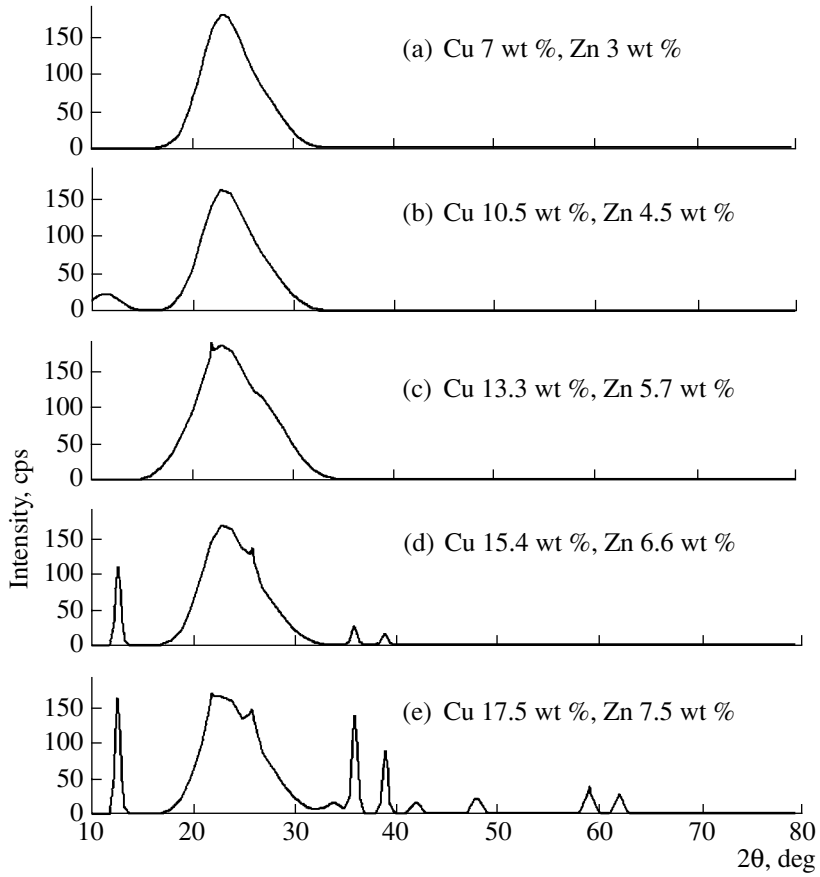

Fig. 8. XRD patterns of CuZn–BD/FSM-16-2 with different metal loadings: (a) 10, (b) 15, (c) 19, (d) 22, and (e) 25 wt %. The catalysts were calcined at 473 K.

Table 2. Catalytic activity and selectivity for methanol steam reforming of CuZn-impregnated catalysts using different kinds of organic compounds during impregnation

Organic compound	Amount of organic compound, 10^{-4} mol/g Cat	Methanol conversion, mol %	Selectivity to CO_2, mol %
Propanol	7.8	0	100
1,3-Butanediol	8.0	41.4	100
1,3-Propanediol	7.0	67.8	100
Ethylene glycol	7.2	70.6	100
Citric acid	8.0	35.5	100

Note: Metal content (Cu + Zn) = 10 wt %; Cu : Zn = 7 : 3; catalysts were calcined at 773 K for 3 h.

seen that all the catalysts modified with 1,3-BD, 1,3-PD, EG, and citric acid enhanced the methanol conversion, while the one modified by propanol did not. This could be explained by suggesting that propanol has lower coordination ability than the others. This suggestion would be supported by the work performed by White *et al.* [23], who studied the effect of alcohols and polyethylene glycols added during preparation of alumina from aluminum nitrate with aqueous ammonia. Their work showed that the addition of low-boiling-point alcohol has little effect on the properties of alumina because the adsorption of additives on the precipitate is not strong enough to allow the replacement of adsorbed water. However, it is theorized that high-boiling-point solvent of strong complexing ability remains around the particles even after elimination of physical adsorbed water during drying until its decomposition on calcinations. It could be suggested that the role of the diols and citric acid used in this study is to distribute the metal ion in the solution by replacing the coordinated water around the metal ion. Moreover, the diols and citric acid probably formed an H bond with the silanol group on FSM-16, and this resulted in an improvement of dispersion and activity. Further study on the role and relationship of the organic ligand to the metal and surface of the support is currently being carried out.

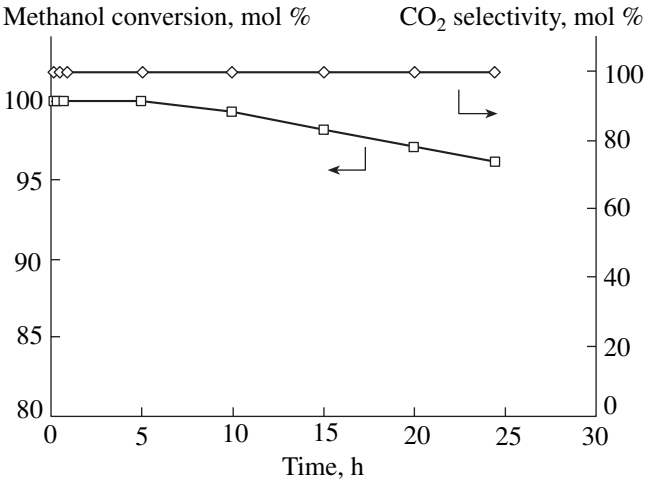

Fig. 9. Time on stream experimental result on CuZn–BD/FSM-16-2 with 22 wt % metal loading (Cu, 15.4 wt %; Zn, 6.6 wt %). The catalysts were calcined at 473 K.

4. CONCLUSIONS

Catalytic activity in steam reforming of methanol over copper- and zinc-impregnated FSM-16 can be improved by modification with 1,3-butanediol. The enhancement in activity is attributed to the improvement of Cu dispersion. The amount of 1,3-butanediol used affected the catalytic activity of the catalyst. The maximum conversion was obtained when 5.3×10^{-4} mol/g Cat of 1,3-butanediol was used. The modified catalyst with 22 wt % metal calcined at 473 K gave the highest methanol conversion. Besides 1,3-butanediol, modification with an organic compound like 1,3-propanediol, ethylene glycol, and citric acid also resulted in an enhancement in catalytic activity, while propanol did not result in any enhancement.

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